



# Selective conversion of glycerol to hydroxyacetone in gas phase over $\text{La}_2\text{CuO}_4$ catalyst



Mauricio Velasquez<sup>a,b</sup>, Alexander Santamaria<sup>a</sup>, Catherine Batiot-Dupeyrat<sup>b,\*</sup>

<sup>a</sup> University of Antioquia, Química de Recursos Energéticos y Medio Ambiente, Instituto de Química, Facultad de Ciencias Exactas y Naturales, Universidad de Antioquia UdeA, Calle 70 No. 52-21, Medellín, Colombia

<sup>b</sup> IC2MP, UMR CNRS 7285, ENSIP, Université de Poitiers, 1 rue Marcel Doré, 86073 Poitiers Cedex 9, France

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## ABSTRACT

The gas phase dehydration of glycerol to hydroxyacetone was investigated over  $\text{La}_2\text{CuO}_4$  catalyst under inert conditions. The reaction was performed in the temperature range of 260–400 °C. At low temperature (260 and 280 °C) high yields of hydroxyacetone can be achieved: 76% while at higher temperatures carbon deposition occurred. We showed that the structure of the  $\text{La}_2\text{CuO}_4$  catalyst was modified during time on stream:  $\text{Cu}^{2+}$  was partially reduced into  $\text{Cu}^{1+}$  even at 260 °C. The formation of  $\text{Cu}_2\text{O}$  was revealed by XRD and XPS analysis confirmed that both  $\text{Cu}^{2+}$  and  $\text{Cu}^{1+}$  are present at the surface of the catalyst. After reduction of  $\text{La}_2\text{CuO}_4$  into  $\text{Cu}^0/\text{La}_2\text{O}_3$ , low catalytic activity was observed proving that metallic copper is not the required species to perform the dehydration of glycerol into hydroxyacetone under our experimental conditions. TGA analysis revealed that only small amount of carbon deposition occurred during time on stream at 260 °C, no catalytic deactivation being observed during 20 h of reaction.

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## 1. Introduction

Glycerol is the main by-product obtained in the production of biodiesel from transesterification of vegetable oils and fats, so there are needs for its valorization. A large number of high added value products can be formed from glycerol reduction or oxidation using heterogeneous or homogeneous catalysts in liquid or gas phase [1].

The hydrogenolysis of glycerol to 1,2 or 1,3 propanediol was largely described in liquid phase under hydrogen pressure [2–5]. In gas phase, glycerol was successfully converted into acrolein over solid acid catalysts such as heteropoly acids [6] or zeolites [7]. The production of acrolein is often accompanied by the formation of hydroxyacetone (HA), which is an interesting chemical product used as flavour in food industry, dyes, additive in cosmetics.

Therefore there are needs to produce selectively HA under mild experimental conditions, in a fixed bed continuous flow process at atmospheric pressure. Different metal oxides were used to perform the dehydration of glycerol in gas phase:  $\text{MO}_x$ – $\text{Al}_2\text{O}_3$ – $\text{PO}_4$  [8]. The acid base properties of the catalysts were modified by the addition of Na, K, Co... oxides [9,10]. The mechanisms of glycerol dehydration to hydroxyacetone over Lewis acid sites were proposed by Alhanash et al. [11]. They showed that the terminal OH group of

glycerol interact more likely with Lewis acid site than the internal OH group leading to the formation of 2,3-dihydroxypropene which is then tautomerized to yield HA.

Copper-based catalysts such as copper chromite [12] or  $\text{Cu}/\text{Al}_2\text{O}_3$  [13] were used to perform the dehydration of glycerol to HA. Copper was preferred to nickel or cobalt due to its lower activity for C–C bond cleavage. The major drawback of the gas-phase dehydration of glycerol on acid catalyst is the catalyst deactivation due to coke deposition [14].

Over basic catalyst the mechanism is still under debate, the reaction can proceed directly through dehydration or by dehydrogenation as initial step [15–17].

High selectivity to HA was achieved using 5% Na doped  $\text{CeO}_2$  at 350 °C, but a poor stability was observed with a rapid deactivation with time on stream [18].

In a previous paper we showed that a basic catalyst such as  $\text{LaNiO}_3$  can lead to the formation of hydroxyacetone with acceptable yields at 400 °C [19]. However the production of HA was accompanied with the formation of other products such as ethylene glycol, 1,2 propanediol, methanol, propionaldehyde... and also  $\text{CO}_x$ .

The present study, focuses on the use of a  $\text{La}_2\text{CuO}_4$  catalyst with a related structure called  $\text{K}_2\text{NiF}_4$ -type in which copper is present as  $\text{Cu}^{2+}$ .  $\text{La}_2\text{CuO}_4$  oxide is the only mixed oxide that can be obtained at ambient pressure, the rhombohedral perovskite  $\text{LaCuO}_3$  (with  $\text{Cu}^{2+}$  and  $\text{Cu}^{3+}$ ) being only formed under high oxygen pressures [20]. The

\* Corresponding author. Tel.: +33549453898; fax: +33549453999.

E-mail address: [catherine.batiot.dupeyrat@univ-poitiers.fr](mailto:catherine.batiot.dupeyrat@univ-poitiers.fr) (C. Batiot-Dupeyrat).

glycerol dehydration reaction was investigated in the temperature range: 260–400 °C. Special attention was given to the modification of the catalytic phase during time on stream, and the oxidation state of copper.

## 2. Experimental

### 2.1. Catalyst preparation

The  $\text{La}_2\text{CuO}_4$  and lanthanum oxide ( $\text{La}_2\text{O}_3$ ) were prepared by the self combustion method [21]. In the synthesis,  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Rhodia),  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (Aldrich), and glycine (Merck) were used.

Glycine ( $\text{H}_2\text{NCH}_2\text{CO}_2\text{H}$ ) used as ignition promoter was added to an aqueous solution of metal nitrates with appropriated stoichiometry, in order to get a  $\text{NO}_3^-/\text{NH}_2 = 1$  ratio. The resulting solution was slowly evaporated at  $\sim 100^\circ\text{C}$  until a vitreous green gel was obtained. The gel was heated up to around  $250^\circ\text{C}$ , temperature at which the ignition reaction occurs producing a powdered precursor which still contains some carbon residue. A calcination at  $700^\circ\text{C}$  for 6 h eliminates all of the remaining carbon.

### 2.2. Catalyst characterization

The XPS analyses were carried out with a Kratos Axis Ultra DLD spectrometer using a monochromatic Al K $\alpha$  source (10 mA and 15 kV). The charge Neutraliser system was operated for all analyses. Instrument base pressure was  $9 \times 10^{-8}$  Pa. High-resolution spectra were recorded using an analysis area of  $300 \mu\text{m} \times 700 \mu\text{m}$  and a 20 eV pass energy. These pass energies correspond to Ag 3d5/2 FWHM of 0.55 eV. Data were acquired with 0.1 eV steps. All the binding energies were calibrated with the C1s binding energy fixed at 284.6 eV as an internal reference. Spectra were analysed with CasaXPS software (version 2.3.17) and Gaussian–Lorentzian fitting (profiles). For the quantitative analysis, the following binding energies regions were recorded: C1s, O1s, Cu2p, CuLMM and La3d.

The catalysts were characterized by X-ray diffraction (XRD) using a Siemens D-5005 diffractometer with  $\text{CuK} = 1.5417 \text{ \AA}$ , operated at 40 kV and 30 mA. The diffraction patterns were recorded in the  $2\theta$  range of  $10\text{--}90^\circ$  with a step interval of  $0.02^\circ$  and period of 1 s.

The specific surface areas of the catalysts were determined from adsorption–desorption isotherms of nitrogen at  $-196^\circ\text{C}$  using a Tristar apparatus (Micromeritics) and applying the BET method.

Temperature programmed reduction analyses (TPR) were carried out in a Micromeritics Autochem 2910 equipment using about 100 mg of catalyst. These experiments were performed using 5%  $\text{H}_2/\text{Ar}$  flow while the temperature was raised at  $5^\circ\text{C min}^{-1}$  from ambient to  $900^\circ\text{C}$  and maintained at this temperature for 30 min. Prior to the measurements, the samples were out gassed under helium at  $350^\circ\text{C}$  for 8 h.

Thermogravimetric analysis (TGA) was carried out with a SDT 2960 thermobalance TA Instruments analyser in Pt crucibles to determine the stability of the catalyst. The measurement was performed under an air flow of  $100 \text{ mL min}^{-1}$  on heating from room temperature to  $800^\circ\text{C}$  with a heating rate of  $5^\circ\text{C min}^{-1}$ .

### 2.3. Experimental setup

Catalytic decomposition of glycerol was carried out at atmospheric pressure by passing a continuous flow of 20% v/v pure glycerol in  $\text{N}_2$  as the carrier gas over the catalyst bed, employing a two zone reactor, pure glycerol (99.9%) was vaporized in the first zone before arriving to the reaction zone.

The temperature in the first reactor was maintained at  $300^\circ\text{C}$ , while the temperature in the second reactor was varied between

$260^\circ\text{C}$  and  $400^\circ\text{C}$ . Liquid phase products were recovered by condensation in two cold traps located at the reactor outlet for further analysis, whereas gas phase was analyzed by gas chromatography during the reaction. Separation and quantification of main organic compounds in liquid phase were performed using a gas chromatograph (Varian 430 GC) equipped with a capillary column ( $50 \text{ m} \times 0.25 \times 0.2 \mu\text{m}$ , CP WAX 58 CB) and a FID detector. Quantification was performed by using butanol as internal standard. The products of the glycerol decomposition were identified by GC–MS (Varian 3800, injector 1079) coupled with a mass spectrometer (Analyser triple quadrupole Varian 1200L with an electric impact source of 70 eV).

Pyrvaldehyde and glyceraldehyde also present in liquid phase were analysed by HPLC (Varian 356-LC) equipped with a refractive index detector and UV detector. The separation of products was realized over aICSep ICE-COREGEL-107H column. The quantification was performed using oxalic acid as internal standard.

Conversion of glycerol and product selectivity was calculated according to the following equations:

$$\text{glycerol conversion(\%)} = \frac{\text{mols of glycerol reacted}}{\text{mols of glycerol in the feed}} \times 100$$

$$\text{product } i \text{ selectivity(\%)} = \frac{\text{mols of carbon in } i \text{ product}}{\text{mols of carbon in glycerol reacted}} \times 100$$

The carbon balance was calculated as the sum of product selectivity (in liquid and gas phase).

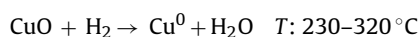
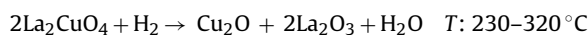
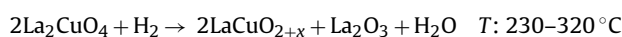
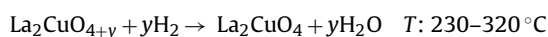
## 3. Results and discussion

### 3.1. Catalysts characterization before reaction

#### 3.1.1. TPR profile of $\text{La}_2\text{CuO}_4$

The catalyst stability under reducing atmosphere was studied by  $\text{H}_2$ -TPR. The TPR profile shows two steps of reduction, the first one in the temperature range  $230\text{--}320^\circ\text{C}$  corresponds to a  $\text{H}_2$  consumption of  $1.8 \text{ mmol g}^{-1}$  and the second one between  $420$  and  $550^\circ\text{C}$  corresponds to  $0.7 \text{ mmol g}^{-1}$ . The first peak is principally attributed to the reduction of  $\text{Cu}^{2+}$  into  $\text{Cu}^{1+}$  leading to the formation of  $\text{Cu}_2\text{O}$ . At low temperature, it is possible to propose a partial reduction of  $\text{La}_2\text{CuO}_4$  to a delafossite-type phase  $\text{LaCuO}_{2+x}$  containing monovalent Cu but also  $\text{Cu}^{2+}$  [22]. This is consistent with the XRD analysis performed after reduction of  $\text{La}_2\text{CuO}_4$  at  $330^\circ\text{C}$  (see Fig. 5c). The high amount of  $\text{H}_2$  consumed at low temperature proves that the reduction of  $\text{Cu}^{2+}$  in  $\text{La}_2\text{CuO}_4$  is not the only reaction that proceeds. It is suggested that  $\text{Cu}^{3+}$ , associated with an excess of oxygen, is present in the compound ( $\text{La}_2\text{CuO}_{4+y}$  with  $0 < y < 0.1$ ) [23]. The reduction of the excess of oxygen in  $\text{La}_2\text{CuO}_{4+y}$  would occurred at low temperature. Moreover it is possible to propose that segregated CuO (not detected by XRD) is formed besides the  $\text{La}_2\text{CuO}_{4+y}$  phase, during the synthesis procedure. This CuO would be reduced at low temperature, which contributes to the higher amount of  $\text{H}_2$  consumed than expected (Fig. 1).

The second step of reduction occurring at higher temperature is ascribed to copper reduction to its metallic state [22,24]. The different reactions involved during the reduction procedure could be summarized as follow:



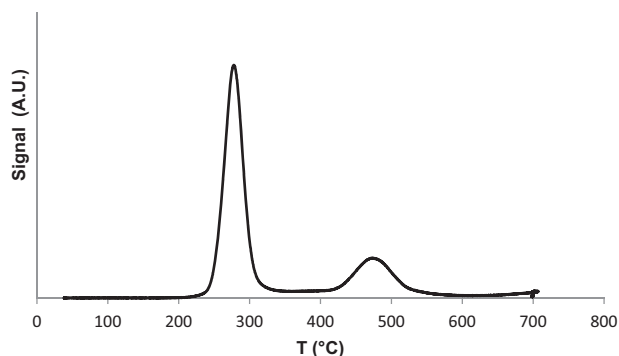
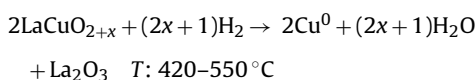
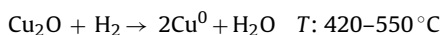


Fig. 1. TPR profile of  $\text{La}_2\text{CuO}_4$ .



### 3.1.2. Influence of the reaction temperature

The transformation of glycerol was investigated in a temperature range between 260 and 400 °C while the catalyst weight was fixed at 1 g and the reaction time at 2.5 h. As shown in Fig. 2, glycerol conversion is the highest at the lowest temperatures and is minimum at 350 °C. When the temperature reaches 400 °C, the conversion of glycerol is higher than at 350 °C due to the formation of gaseous products ( $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{CO}_2$  and  $\text{H}_2$ ) through reforming reactions. The carbon balance profile follows the glycerol conversion, showing that the formation of heavy products is responsible for catalyst deactivation from 300 °C. The formation of such heavy compounds with  $m/z$  up to 1000 was confirmed using MALDI-TOF mass Spectrometer. At 260 and 280 °C, HA selectivity was equal to, respectively, 74.2 and 76.3%. Pyruvaldehyde and glycer-aldehyde were also produced in a significant amount while other products were analysed but in low amount: propionaldehyde, glycidol, 1,3-propanediol, 1-propanol, ethylene glycol, methanol. ... The selectivity to HA drops at 39.4% when the reaction is performed at 300 °C.

The same behavior was observed by Sato et al. [13] using  $\text{Cu}\text{--}\text{Al}_2\text{O}_3$  catalyst, proving that over copper catalyst deactivation proceeds readily as soon as the temperature exceeds 300 °C. The

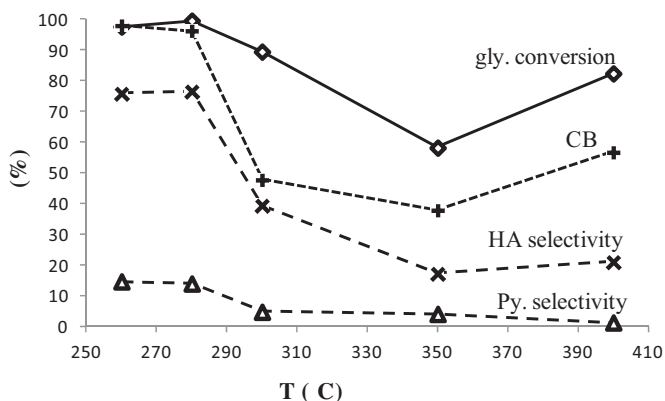


Fig. 2. Influence of the reaction temperature on glycerol conversion and selectivity to products after 2.5 h of reaction. Reaction conditions: 1 g of catalyst, total flow: 33  $\text{mL min}^{-1}$ , 20 vol% glycerol in  $\text{N}_2$  in gas phase. Gly.: glycerol, Py.: pyruvaldehyde, CB: carbon balance.

results obtained in this study and those reported by Sato et al. indicate that it is possible to produce selectively hydroxyacetone using copper based catalysts as soon as the reaction temperature is lower than 300 °C, whatever the nature of the oxide: basic or acid. The influence of copper oxidation state is discussed below.

### 3.1.3. Influence of contact time

The catalyst weight was varied from 50 to 400 mg to observe the influence of contact on the reactivity of glycerol at 280 °C. The shape of the curves giving product yield versus contact time (Fig. 3) shows that hydroxyacetone and glycer-aldehyde appear as primary product, while pyruvaldehyde results from the transformation of primary products. Methanol and ethylene glycol are produced in low yields when the contact time exceeds  $0.2 \times 10^{-3}$  h, these two products are formed from glycer-aldehyde by a C–C bond rupture. However, at such a low temperature the C–C bond scission is not favored, particularly with copper based catalysts. We checked that pyruvaldehyde can be produced either from hydroxyacetone or glycer-aldehyde using different reactant mixtures glycerol + glycer-aldehyde and glycerol + hydroxyacetone. In both cases the amount of pyruvaldehyde formed was increased compared to pure glycerol as reactant. According to the results obtained here the following scheme can be proposed for the conversion of glycerol in gas phase over the  $\text{La}_2\text{CuO}_4$  catalyst (Fig. 4).

Catalysts characterization after reaction and after reduction.

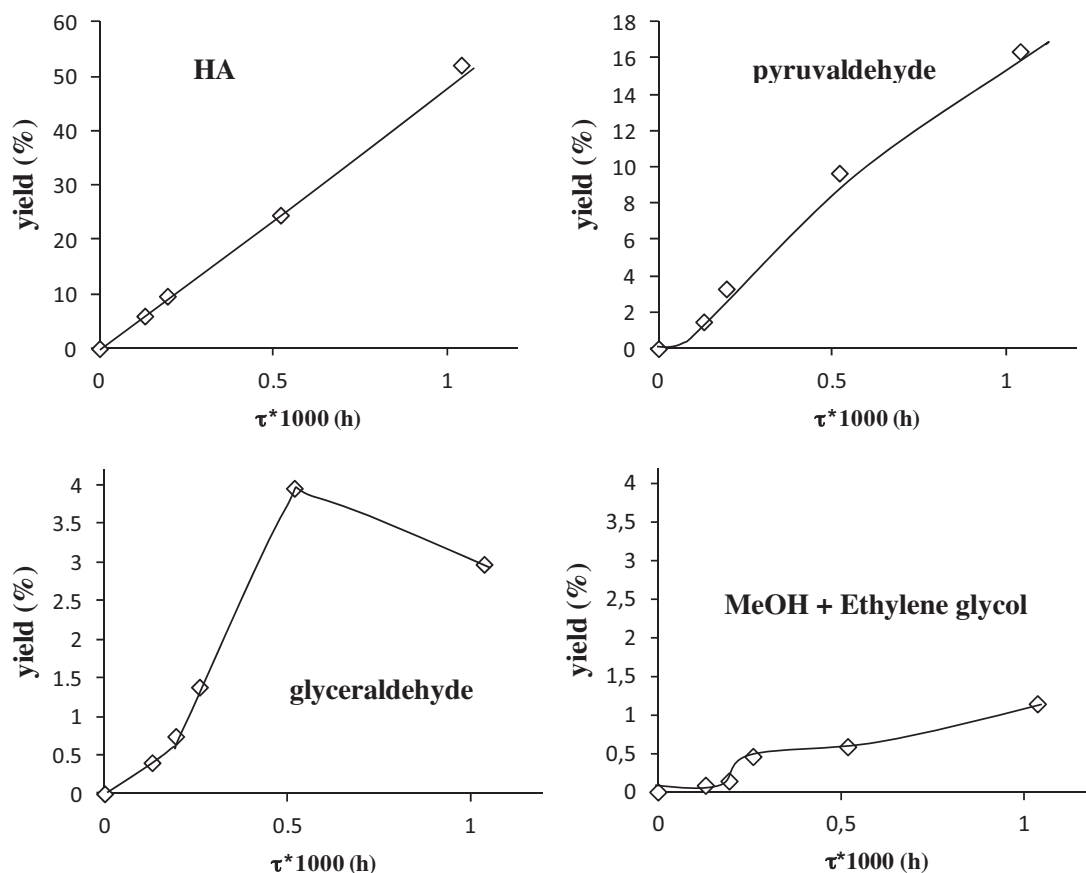
### 3.1.4. XRD analysis

The XRD pattern of the prepared  $\text{La}_2\text{CuO}_4$  catalyst shows diffraction peaks of the orthorhombic perovskite-like  $\text{K}_2\text{NiF}_4$  structure (JCPDS PDF 22-0642).

After 2.5 h of reaction at 260 and 350 °C, the  $\text{La}_2\text{CuO}_4$  phase is no more visible but a mixture of lanthanum oxide, lanthanum hydroxide oxide and lanthanum hydroxide was identified (Fig. 5). Diffraction peaks attributed to  $\text{Cu}_2\text{O}$  were also recorded confirming the reduction of  $\text{Cu}^{2+}$  to  $\text{Cu}^{1+}$  under our experimental conditions. Moreover, the presence of the non-stoichiometric delafossite-type oxide  $\text{LaCuO}_{2+x}$  is proposed suggesting the existence of  $\text{Cu}^+$  but also  $\text{Cu}^{2+}$  [25]. The presence of  $\text{Cu}^+$  can be explained by in-situ reduction of  $\text{Cu}^{2+}$  under hydrogen formed during the reaction, but it can be also attributed to the reduction properties of glycerol according to Jin et al. [26]. X-ray diffraction patterns performed after reduction of the starting catalyst under hydrogen at 330 °C exhibited similar phases as after reaction at 260 °C, except that the presence of lanthanum hydroxide oxide is more visible over the catalyst partially reduced at 330 °C. This observation is in accordance with the work of Neumann et al. who showed the formation of  $\text{LaOOH}$  at around 330 °C [27]. When the reaction is performed at 260 °C intense peaks attributed to  $\text{La}(\text{OH})_3$  were recorded while this phase is less visible after reaction at 350 °C due to the low thermal stability of  $\text{La}(\text{OH})_3$  [27].

### 3.1.5. XPS analysis

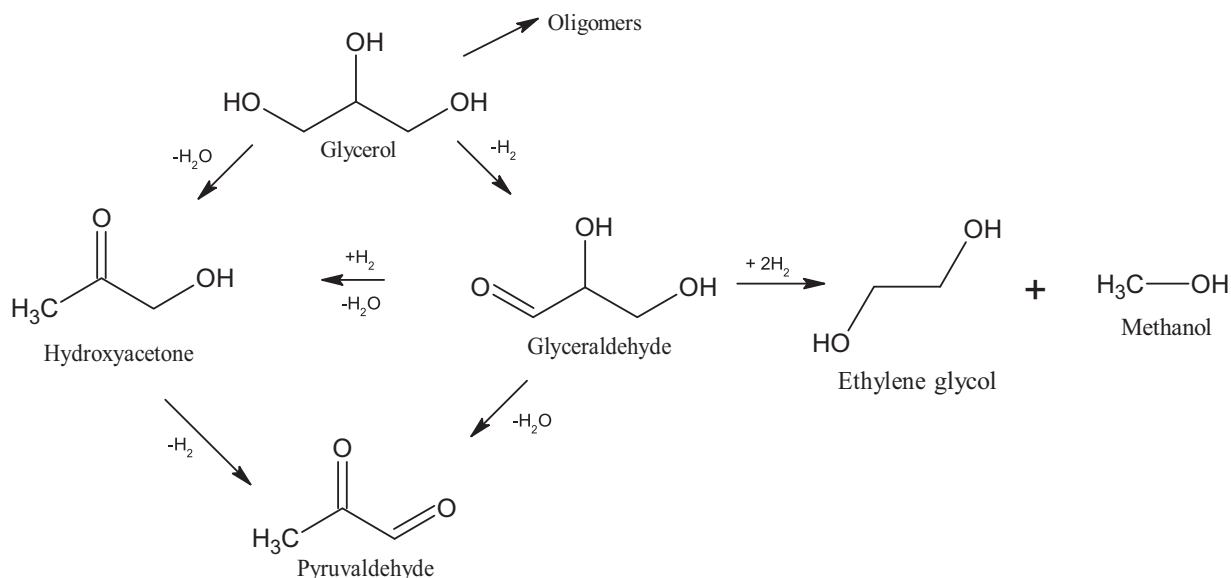
$\text{Cu } 2p_{3/2}$  XPS spectra of the catalysts before and after reaction at 260 °C are shown in Fig. 6. For the fresh  $\text{La}_2\text{CuO}_4$  catalyst, the binding energy corresponding to  $\text{Cu } 2p_{3/2}$  is observed at 933.6 eV. The presence of shake-up satellites peaks at  $\text{BE} = 940.9$  and  $943.3$  eV are the signature of  $\text{Cu}^{2+}$  [28]. After reaction the shift of the main  $\text{Cu } 2p_{3/2}$  peak to 931.7 eV and the significant decrease of the peak intensity of the satellites indicate the formation of reduced copper species. Differentiation between  $\text{Cu}^+$  and  $\text{Cu}^0$  species in XPS is possible through the examination of the Auger parameter [29]. The Auger parameter of copper were recorded using standard sample, the values obtained for copper(II), copper(I) and copper metal were 1851.2, 1848.9 and 1851.2 eV, respectively, consequently  $\text{Cu}^{2+}$  and  $\text{Cu}^0$  are not distinguishable by the Auger parameter. In our case,



**Fig. 3.** Influence of contact time on product yield, reaction conditions: catalyst weight: 50 to 400 mg, total flow: 33 mL.min<sup>-1</sup>, 20 vol% glycerol in N<sub>2</sub> in gas phase T: 280 °C, reaction time: 2.5 h.

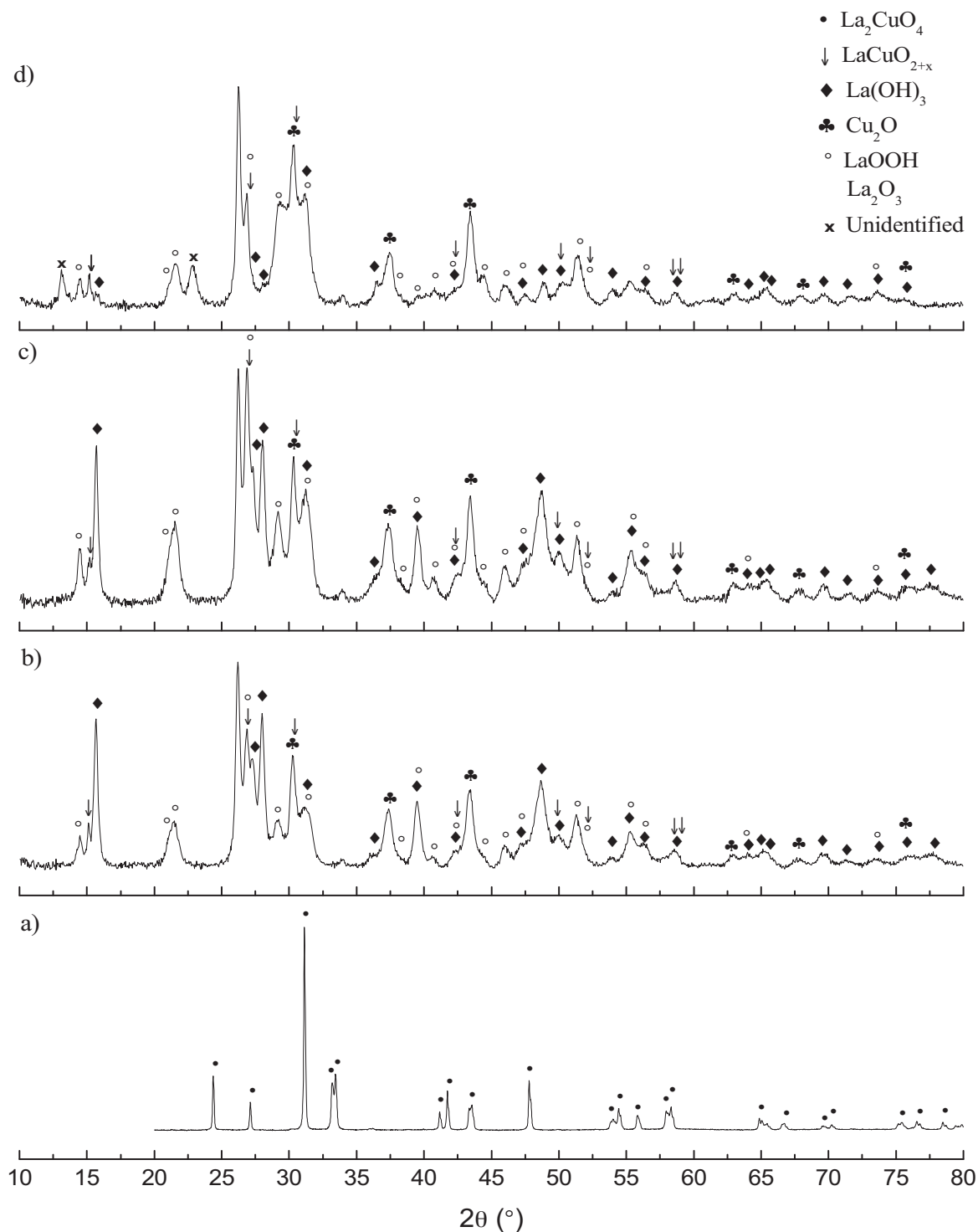
the Auger parameter before reaction was equal to 1851.6 eV, this energy is attributed to the presence of Cu<sup>2+</sup> since metallic copper could not be obtained in the conditions used to prepare the fresh La<sub>2</sub>CuO<sub>4</sub> catalyst (calcination at 700 °C under air). After reaction the Auger parameter is modified giving a value of 1848.9 eV, energy corresponding to Cu<sup>+</sup>. Moreover, the FWHM (1.3) was exactly the

same as Cu<sub>2</sub>O used as reference sample for Cu<sup>1+</sup>. The molar ratio Cu<sup>2+</sup>/Cu<sup>+</sup> determined from peaks decomposition was equal to 0.5 showing that the surface of the catalyst after reaction is mostly composed of Cu<sup>+</sup>. This result is in accordance with XRD spectra performed after reaction which indicates the formation of Cu<sub>2</sub>O and LaCuO<sub>2+x</sub> during the reaction.



**Fig. 4.** Possible reaction pathways from glycerol to hydroxyacetone, glyceraldehyde and pyruvaldehyde.

a) before reaction b) after reaction at 260°C c) after reduction at 330°C d) after reaction at 350°C



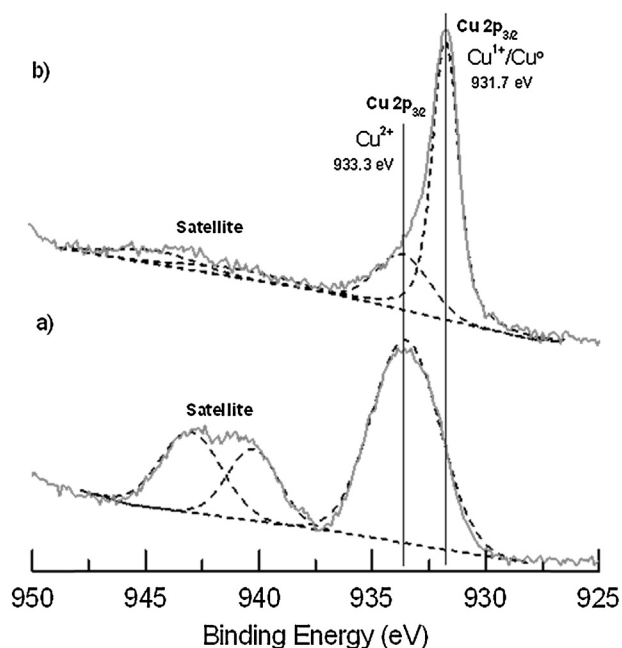
**Fig. 5.** XRD patterns of  $\text{La}_2\text{CuO}_4$  before and after 2.5 h of reaction at 260 and 350 °C, (a) before reaction (b) after reaction at 260 °C (c) after reduction at 330 °C (d) after reaction at 350 °C.

### 3.1.6. TGA analysis

Thermogravimetric analysis coupled with mass spectra was performed after 2.5 h of reaction at 260 and 350 °C (Fig. 7). Wide variations were observed in the weight profiles depending on the

reaction temperature used. The weight loss between 150 and 300 °C observed after reaction at 260 °C can be assigned to the presence of strongly adsorbed reactant and products at the surface of the catalyst (glycerol, hydroxyacetone...). This weight loss is less visible

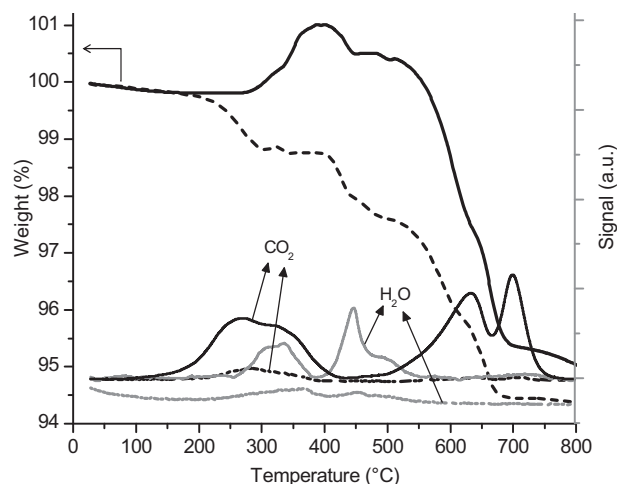




**Fig. 6.** XPS analysis of La<sub>2</sub>CuO<sub>4</sub> before reaction (a) after reaction at 260 °C during 2.5 h (b).

when the reaction is observed at 350 °C due to the less favorable adsorption of organic products at such a temperature. From 300 to 410 °C, there is a weight increase attributed to the oxidation of copper +1 to Cu<sup>2+</sup>. The weight gain is equal to 1.2% after reaction at 350 °C while it corresponds to only 0.04% after reaction at 260 °C. However it is not possible to propose a quantification of oxygen gain in the material due to probable compensation of the phenomena of oxidation and removal of surface carbon species as shown on mass spectra profiles.

The mass losses between 410 and 450 °C is attributed to the transformation of La(OH)<sub>3</sub> to successively LaOOH and La<sub>2</sub>O<sub>3</sub> [27]. The dehydration of La(OH)<sub>3</sub> is confirmed by mass spectra analysis showing the release of water in the temperature range, while no CO<sub>2</sub> was detected. The largest weight loss is obtained at higher temperatures, between 550–620 and 620–700 °C these weight losses can be ascribed to carbonaceous deposits. The spent samples used at 350 °C presented 5.5% weight loss while the catalyst used at 260 °C shows a weight loss of 3%.

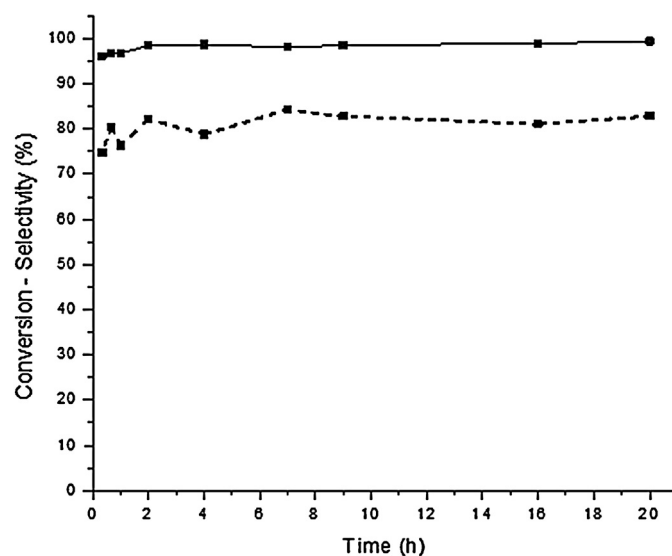


**Fig. 7.** Thermogravimetric analysis coupled with mass spectrometry after 2.5 h of reaction at 260 °C (dashed lines) and 350 °C (straight lines).

### 3.1.7. Discussion on reaction route to hydroxyacetone from glycerol

The exact role of catalytic species: acid/basic sites and redox properties of metal oxides for hydroxyacetone formation is still under debate in the literature. It is often proposed that the first step is the dehydrogenation of glycerol into glyceraldehyde at the metal surface followed by its dehydration and enolization on the oxide support [18]. Over basic catalysts, Stosic et al. [16] suggest that either direct dehydration or dehydrogenation as first step can occur.

In order to investigate the role of copper and its oxidation state in the transformation of glycerol, experiments were performed at 280 °C after partial or complete reduction of La<sub>2</sub>CuO<sub>4</sub>. The results obtained with La<sub>2</sub>CuO<sub>4</sub> without reduction were also compared with those obtained with La<sub>2</sub>O<sub>3</sub> (Table 1). The reduction of La<sub>2</sub>CuO<sub>4</sub> was performed at 330 °C, temperature at which Cu<sup>1+</sup> is formed (Fig. 5c), and at 600 °C to obtain Cu<sup>0</sup>/La<sub>2</sub>O<sub>3</sub> (see TPR profiles). The differences observed in the catalytic activities cannot be attributed to textural properties modification since the catalyst possesses very low surface area (about 2 m<sup>2</sup> g<sup>−1</sup>) not modified by the reduction treatment. The best catalytic activity is reached when the catalyst is not reduced prior to the reaction, showing unambiguously that metallic copper species are not required to perform the reaction. Over the catalyst reduced at 330 °C prior to the reaction, the catalytic activity is lower than over the non-reduced material proving that Cu<sup>1+</sup> species, generated under hydrogen treatment, are less active than the partially reduced species formed from La<sub>2</sub>CuO<sub>4</sub> during time on stream. As shown by XRD analysis, after hydrogen treatment at 330 °C, the partially reduced species are present in the form of Cu<sub>2</sub>O and LaCuO<sub>2+x</sub> associated with LaOOH, La(OH)<sub>3</sub> and La<sub>2</sub>O<sub>3</sub>. The nature of phases present after reduction at 330 °C and after reaction at 260 °C are similar but it seems that the amount of the respective phases differ significantly which could explain the differences observed in the catalytic activity. The activity of Cu<sub>2</sub>O was investigated using a commercial oxide under the same reaction conditions. Results show that Cu<sup>1+</sup> is active for the dehydration of glycerol but the catalytic activity of Cu<sub>2</sub>O is lower than La<sub>2</sub>CuO<sub>4</sub>. Consequently, it is possible to state that Cu<sup>1+</sup> in Cu<sub>2</sub>O is active but the interaction between lanthanum and copper favors the reaction. It is interesting to note that the activity of the reduced La<sub>2</sub>CuO<sub>4</sub> catalyst (corresponding to Cu<sup>0</sup>/La<sub>2</sub>O<sub>3</sub>) is approximately



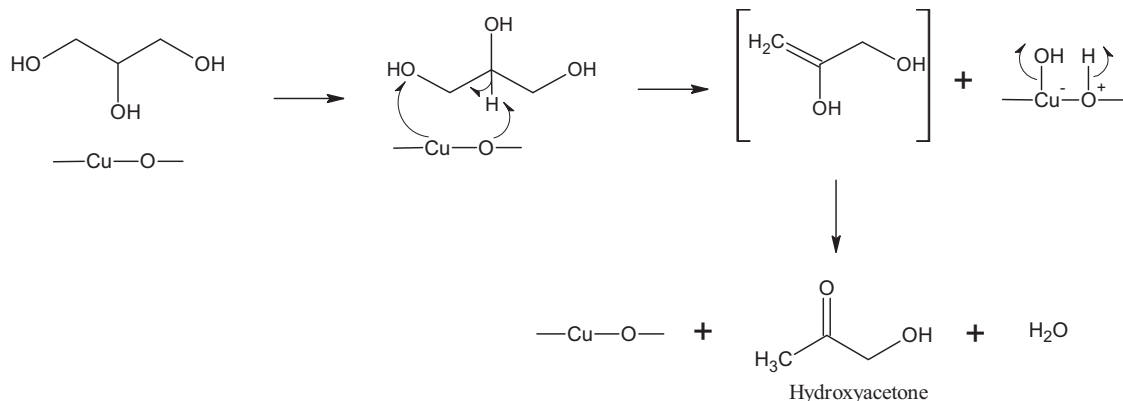
**Fig. 8.** Catalytic stability, La<sub>2</sub>CuO<sub>4</sub> without reduction, 1 g of catalyst,  $T = 260$  °C, total flow: 33 mL min<sup>−1</sup>, 20 vol% glycerol in N<sub>2</sub> in gas phase. Conversion (straight lines), hydroxyacetone selectivity (dashed lines).

**Table 1**  
Glycerol conversion on  $\text{La}_2\text{CuO}_4$  and  $\text{La}_2\text{O}_3$  catalysts at  $280^\circ\text{C}$ .

Catalyst	Reduction temperature ( $^\circ\text{C}$ )	X (%)	HA yield (%)	Selectivity (%)			Carbon balance (%)
				HA	Pyrvaldehyde	Glyceral.	
$\text{La}_2\text{CuO}_4$	No	99.6	76.3	76.6	13.9	2.5	96.3
$\text{La}_2\text{CuO}_4$	330	93.0	43.7	47.0	16.9	4.2	70.9
$\text{La}_2\text{CuO}_4$	600	42.1	5.5	13.1	4.2	2.7	24.0
$\text{La}_2\text{O}_3$	No	43.0	7.1	16.5	6.5	1.2	44.9
$\text{La}_2\text{CuO}_4^*$	No	42.0	14.4	34.2	22.7	4.9	58.6
$\text{Cu}_2\text{O}$	No	72.3	35.9	49.6	21.3	2.0	75.2

Reaction conditions: 1 g catalyst, total flow:  $33\text{ mL min}^{-1}$ ,  $T = 280^\circ\text{C}$ , 20% glycerol in  $\text{N}_2$  in gas phase, X = glycerol conversion, HA: hydroxyacetone, Glyceral.: glyceraldehyde 2.5 h of reaction.

\* Catalyst weight: 80 mg.



**Fig. 9.** Proposed mechanism of hydroxyacetone formation from glycerol on  $\text{La}_2\text{CuO}_4$  as starting catalyst.

the same as  $\text{La}_2\text{O}_3$ , proving that metallic copper is not active for the dehydration of glycerol under our experimental conditions. The carbon balance indicates that the presence of metallic copper favors the carbon deposition and thus the catalyst deactivation. The unreduced  $\text{La}_2\text{CuO}_4$  is much more active than  $\text{La}_2\text{O}_3$  since only 80 mg of catalyst are necessary to reach the same glycerol conversion as 1 g of  $\text{La}_2\text{O}_3$ . Comparing data from the literature obtained in similar reaction conditions (temperature around  $260^\circ\text{C}$ , gas phase...), it seems that metallic copper is active to produce HA as soon as an acidic support is used such as  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{Fe}_2\text{O}_3$  or  $\text{SiO}_2$ . Over a basic support such as  $\text{MgO}$ ,  $\text{CeO}_2$ ,  $\text{ZnO}$  or  $\text{La}_2\text{O}_3$  (this work) the catalytic activity is low most probably due to deactivation by carbon deposition. Using copper based oxides without reduction step prior to the reaction, acid support leads to deactivation with time on stream [13] while over a basic oxide like  $\text{La}_2\text{CuO}_4$  high catalytic activity can be maintained. The reaction was prolonged during 20 h at  $260^\circ\text{C}$ , the glycerol conversion and the selectivity to hydroxyacetone were maintained at their high level (Fig. 8).

Consequently according to the results obtained here it is possible to propose a reaction scheme in which a concerted mechanism occurs between copper and an oxygen ion (Fig. 9). In this scheme a primary OH group is released leading to the formation of an unstable enol intermediate, which undergoes rapid rearrangement to hydroxyacetone. A similar mechanism was proposed over the perovskite  $\text{LaNiO}_3$  at higher temperature ( $400^\circ\text{C}$ ) in a previous paper [19]. The catalyst  $\text{LaNiO}_3$  was almost inactive in the experimental conditions used in this study ( $T$ :  $260$ – $280^\circ\text{C}$ , 1 g of catalyst), confirming the major role of copper for the conversion of glycerol to hydroxyacetone.

#### 4. Conclusion

The catalyst  $\text{La}_2\text{CuO}_4$  exhibits a very high activity and stability for the conversion of glycerol to hydroxyacetone, a yield of more

than 75% being obtained at  $260^\circ\text{C}$  without catalyst deactivation during 20 h of reaction. At higher temperature (from 300 to  $400^\circ\text{C}$ ), the catalytic activity is low most probably due to carbon deposition according to TGA experiments. The characterization of the catalyst after reaction reveals a phase modification during time on stream:  $\text{Cu}^{2+}$  is partially reduced into  $\text{Cu}^{1+}$ . The presence of metallic copper species is not required to perform the reaction and  $\text{La}_2\text{CuO}_4$  is much more active than the simple  $\text{La}_2\text{O}_3$  oxide. A concerted mechanism is proposed between copper and a basic site of the support to explain the formation of hydroxyacetone from glycerol.

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